

**FABRICATION AND CHARACTERIZATION OF BIODEGRADABLE
FILMS FROM SAWDUST**

NOR HAFIZA BINTI HAMIDON

**A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering**

**Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang**

APRIL 2009

DECLARATION

I declare that this thesis entitled “Fabrication and Characterization of Composite Biodegradable Films from Sawdust” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

Signature :.....

Name : Nor Hafiza bt Hamidon

Date : 20 APRIL 2009

DEDICATION

To my beloved Mum,
My family members that always love me,
My friends, my fellow colleague
My supervisor,
And all faculty members,

For all your care, support and believe in me.

Love,
Nor Hafiza Hamidon

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,

I am so thankful to Allah S.W.T for giving me patient and spirit throughout this project until the research is successfully complete. With the mercifulness from Allah therefore I can produces a lot of useful idea to this project.

To my beloved mother, Latifah Abu Bakar, I am grateful to have you in my life and giving me full of support to through this life. I pray and wish you are always in good health and Allah mercy. You are the precious gift from Allah to me.

I am indebted to my supervisor, Madam Norashikin bt Mat Zain, lecturer from the Faculty of Chemical and Natural Resources Engineering for her advice, insightful comments and support. Thank for your guide and without your guide this research will not be complete and well organized. And not forgetting for my panels, Mrs Noor Ida Amalina bt Ahmad Nordin and Prof Ir Dr Jailani bin Salihon for your brilliant ideas that you gave to me, thank you.

I would also like to thank to all my beloved friends especially Azliya Abd Rahman, Lim Rwi Hau, Mohd Faizan Jamaluddin, Zulsyazwan Ahmad Khushairi, and Junaidi Zakaria who have accompanied throughout this project. Thank you very much.

ABSTRACT

This report shows the performance of the composite biodegradable film using chitosan as a primary material with addition sawdust fiber and starch as polymer matrix. The main objective of this research is to fabricate the composite biodegradable film using chitosan with sawdust fiber (CS) and the composite biodegradable film using chitosan, starch and sawdust fiber (CSS). The films were prepared by wet casting of the aqueous solution containing chitosan as the main polymer, acetic acid 1% v/v as solvent, PEG 400 as plasticizer. Sawdust was used as fiber and starch as matrix polymer were added in the chitosan solutions. The solutions were poured on a glass plate and dry it in ambient temperature. The films morphology structure was observed using Atomic Force Microscopy (AFM). The results revealed that the CS film more smooth and good integrity structure. Chemical composition of the films was investigated using Fourier Transform Infrared (FTIR) and revealed the starch presence in CSS film. The thermal properties characterization using Thermal Gravimetric Analyzer (TGA) and Differential Scanning Calorimetric (DSC) showed that thermal properties for both films are not quite different in melting and degradation temperature.

ABSTRAK

Kajian ini menunjukkan pencapaian filem campuran yang mampu dibiodegradasi yang dibuat dengan *chitosan* sebagai bahan utama dengan tambahan hampas serbuk kayu sebagai gentian dan kanji sebagai polimer cetak. Tujuan utama kajian ini adalah untuk menghasilkan filem campuran menggunakan *chitosan* dengan serbuk kayu (CS) dan filem campuran menggunakan *chitosan*, kanji dan serbuk kayu (CSS). Filem ini diperbuat menggunakan kaedah acuan lembap larutan akueus daripada campuran *chitosan* sebagai polimer utama, asid asetik 1% v/v sebagai pelarut dan *PEG 400* sebagai bahan pengenyal. Serbuk kayu digunakan sebagai gentian dan kanji sebagai polimer cetak yang dicampurkan di dalam larutan *chitosan*. Larutan dituangkan ke atas plat kaca dan dikeringkan dengan suhu bilik. Struktur tatabentuk filem dikaji menggunakan *Atomic Force Microscopy (AFM)*. Hasilnya menunjukkan permukaan filem CS lebih lembut strukturnya dan kemas. Campuran bahan kimia bagi filem dikaji dengan menggunakan *Fourier Transform Infrared (FTIR)* dan daripada graf membuktikan kewujudan kanji di dalam filem CSS. Analisa terhadap haba pula menggunakan *Thermal Gravimetric Analyzer (TGA)* dan *Differential Scanning Calorimetric (DSC)*. Hasilnya kedua-dua filem mempunyai sifat kehabaan yang tidak banyak berbeza pada suhu pencairan dan suhu degradasi.

TABLE OF CONTENT

CHAPTER	TITLE	PAGE
	TITLE PAGE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENT	vii
	LIST OF SYMBOL	x
	LIST OF TABLES	xi
	LIST OF FIGURES	xii
1	INTRODUCTION	1
	1.1 Project Background	1
	1.2 Problem Statement	3
	1.3 Objective	3
	1.4 Research Scope	4
2	LITERATURE	5
	2.1 Composite	5
	2.2 Matrix	6
	2.3 Biodegradable Composites & Packaging Film	7
	2.4 Biodegradable Film Preparation	9
	2.5 Characterization of Biodegradable Film	11
	2.5.1 Atomic Force Microscopy (AFM)	11
	2.5.1.1 Principle of AFM	12

2.5.2	Fourier Transform Infrared (FTIR)	13
2.5.3	Differential Scanning Calorimeter (DSC)	15
2.5.4	Thermo Gravimetric Analysis (TGA)	17
2.6	History of Chitosan	18
2.6.1	Overview of Chitosan	20
2.6.2	Application of Chitosan	21
2.7	Overview of Starch	22
2.7.1	Rice Starch	25
2.7.2	Rice Starch Characteristics	25
.....2.7.2.1	Granule Size and Color	25
.....2.7.2.2	Nutritional Qualities	26
2.7.2.3	Flavor Release	
2.7.2.4	Gel Characteristics	
2.8	Natural Fiber	26
2.8.1	Properties of Natural Fiber	27
2.8.2	Sawdust	28
2.8.2.1	Structure, Composition & Properties	29
2.8.2.2	The Need for Sawdust Modification	31
2.8.2.3	Sawdust and Plastic Composites	32
2.9	Application and Historical Development in Sawdust-Plastic Composites	34
2.10	Polyethylene Glycol (PEG)	35
2.11	Acetic Acid	36
3	METHODOLOGY	39
3.1	Raw Materials & Equipment	39
3.1.1	Chitosan	39
3.1.2	Sawdust	40
3.1.3	Isolation of Fiber	40
3.2	Matrix Polymer	41
3.3	Plasticizers	41
3.4	Films preparation	42
3.4.1	Isolation of Fiber	42

3.4.2	Gelatinization of Rice Powder	43
3.4.3	Mixing Process	44
3.4.4	Film Formation	44
3.5	Film Characterization	45
3.5.1	Atomic Force Microscopy (AFM)	46
3.5.2	Fourier Transform Infrared (FTIR)	46
3.5.3	Thermal Gravimetric Analyzers	47
3.5.4	Differential Scanning Calorimeter (DSC)	47
4	RESULT & DISCUSSION	48
4.1	Atomic Force Microscopy	48
4.2	Fourier Transform Infrared	51
4.3	Differential Scanning Calorimetric	53
4.4	Thermo Gravitation Analyzer	54
5	CONCLUSION & RECOMMENDATION	56
5.1	Conclusion	56
5.2	Recommendations	57
	REFERENCE	58

LIST OF SYMBOLS

CS	Chitosan and Sawdust
CSS	Chitosan, Starch and Sawdust
PEG	Polyethylene Glycol
AFM	Atomic Force Microscopy
wt %	weight percent
Ra	means roughness
ρ	Density
μ	Fluid viscosity
ρ_l	Liquid density
ΔH	Enthalpy changes, duty
ΔH_l	Enthalpy for liquid
ΔH°_f	Standard heat of formation
ΔH°_{vap}	Standard heat of vaporization
ΔH_v	Enthalpy for vapor
ΔH_{vap}	Heat of vaporization
ΔP	Pressure differential or pressure drop
C_p	Vapor heat capacity
F	Molar flow rate
g	Gravity acceleration
H	Enthalpy
MW	Molecular weight
P	Pressure
Q	Duty or heat transferred per unit time
T	Temperature

LIST OF TABLE

TABLE NO	TITLE	PAGE
3.1	The amount of substances for preparing the solution	42
4.1	Roughness parameter of CS and CSS composite biodegradable films.	50

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	The carbon cycle of biodegradable polymers	9
2.2	Principle of Atomic Force Microscopy	12
2.3	Basic structure of polymers	15
2.4	DSC TAQ-500 in Analytical Lab, FKKSA Laboratory, UMP	16
2.5	TGA TAQ-500 in Analytical Lab, FKKSA Laboratory, UMP	18
2.6	Chemical structure of Chitosan	20
2.7	Chemical structure of Starch	24
2.8	Diagram showing the relative amounts of cellulose, hemicellulose, and lignin a cross section of two Sawdust cells	31
2.9	Stoichiometric the production of acetic acid from vinegar	36
3.1	Chitosan	39
3.2	Sawdust	40
3.3	Polyethylene Glycol 400	41
3.4	Isolation of sawdust fiber	43
3.5	Gelatinization of rice powder	43
3.6	Mixing Process	44
3.7	Degassed under pressure	45
3.8	Film formation	45
3.9	Fourier Transform Infrared analysis	46
3.10	Differential Scanning Analyser	47
4.1	Series of AFM topographic images of chitosan, and sawdust biodegradable films	48
4.2	Series of AFM topographic images of chitosan, starch with sawdust (CSS) composite biodegradable films	49

4.3	FTIR spectra of (a) CS film, and (b) CSS film	51
4.4	DSC thermograms for (a) CS film and (b) CSS film	53
4.5	TGA curves for CS film (a) and CSS film (b)	54

CHAPTER 1

INTRODUCTION

1.1 Project Background

Food packaging, an important discipline in the area of food technology, concerns preservation and protection of all types of foods and their raw materials, as well from oxidation and microbial spoilage. Petrochemical based plastics such as polyolefin, polyesters, polyamides, etc. have been increasingly used as packaging materials, because of their availability in large quantities at low cost and favorable functionality characteristics such as good tensile and tear strength, good barrier properties to O₂ and aroma compounds and heat sealability.

On the contrary they have a very low water vapor transmission rate and most importantly they are totally non-degradable, and therefore lead to environmental pollution, which pose serious ecological problems. Hence, their use any form or shape has to be restricted and may be even gradually abandoned to circumvent problems concerning waste disposal (Tharanathan and Saroja, 2001). Of late, there is a paradigm shift imposed by the growing environmental awareness by all to look for packaging films and processes, which are biodegradable and therefore compatible with the environment.

In a sense, biodegradability is not only a functional requirement but also an important environmental attribute. Thus, the concept of biodegradability enjoys both user-friendly and eco-friendly attributes, and raw materials are essentially derived

from either replenishable agricultural feedstock or marine food processing industry wastes, and therefore it capitalizes on natural resource conservation with an underpinning on environmentally friendly and safe atmosphere (R.N.Taranathan, 2003). An additional advantage of biodegradable packaging materials is that on biodegradation or disintegration and compositing they may act as fertilizer and soil conditioners, facilitating better yield of the crops.

Commonly it is the most important in the food industry to extend the storage time of food. Up to now, artificially synthesized additives of preservatives have been added to food directly or indirectly to improve the storage stability of food. However, such additives which are harmful to human bodies may exert a bad influence to health as well as peculiar flavor and fragrance of foods. Therefore, there is an urgent need for a method of extending food storage time without using a preservative.

In order to overcome the foregoing problems, research for developing antibacterial packaging film is being actively conducted. It is general that the antibacterial packaging film provides antibacterial property to the packaging material according to types of added antibacterial substances and preparations methods. Particularly, the antibacterial effect, maintenance and properties of the packaging material can vary depending on interaction between the used antibacterial substances and high molecules, which is the main component of the film construction.

Use plastics in cooking and food storage can carry health risks, especially when hormone-disrupting chemicals from some plastics leach into foods and beverages. Plastic manufacturing and incineration creates air and water pollution and exposes workers to toxic chemicals. Designing biodegradable packaging alternatives and ensuring that they end up in an appropriate disposal system can enhance the environmental quality of many products.

1.2 Problem Statement

Food packaging is concerned with the preservation and protection of all types of foods and their materials, particularly from oxidative and microbial spoilage and also to extend their shelf-life characteristics. The rational to do this research is to decrease the environmental pollution from non-biodegradable plastics. Increased use of synthetic packaging films has led to serious ecological problems due too their total non-biodegradability. Continuous awareness by one and all towards environmental pollution by the latter and as result the need for a safe, eco-friendly atmosphere has led to a paradigm shift on the use of biodegradable materials, especially from renewable agriculture feedstock and marine food processing industry wastes. A solution to this problem might be replacing the synthetic packaging plastics with active biodegradable plastics. So, the natural materials are using for developing the biodegradable film or packaging such as chitosan starch or sawdust. Also, the significant of this research is to decrease the use of synthesis additives and preventives for food stability and for developing antimicrobial packaging film.

1.2 Objective

- a. To fabricate the sawdust composite biodegradable films with and without starch
- b. To characterize the different composite biodegradable films using:
 - i. Atomic Force Microscopy (AFM) for morphology characterization
 - ii. Fourier Transform Infrared (FTIR) for chemical composition characterization.
 - iii. Differential Scanning Calorimetric (DSC) and Thermal Gravimetric Analyzer (TGA) for thermal properties characterization.

1.4 Research Scope

The main scopes of this research are:

- a. Fabrication two composite biodegradable films using chitosan with sawdust (CS) and chitosan, starch with sawdust (CSS)
- b. Morphology or structure characterization using Atomic Force Microscopic (AFM),
- c. Chemical composition characterization using Fourier Transform Infrared (FTIR),
- d. Thermal properties characterization of the films using Thermal Gravimetric Analyzer (TGA) and Differential Scanning Calorimetric (DSC).

CHAPTER 2

LITERATURE REVIEW

2.1 Composite

A composite material is a materials system composed of a suitably arranged mixture or combination of two or more micro- or macroconstituents with an interface separating them that differ in form and chemical composition and are essentially insoluble in each other. The engineering importance of a composite material is that two or more distinctly different materials combine to form a composite material that possesses properties that are superior, or important in some other manner, to the properties of the individual components (Smith *et al.*, 2000)

Thus composites are those materials formed by aligning extremely strong and stiff constituents such as fibers and particulates in a binder called matrix. The materials in this class have exceptional mechanical properties. One of the components is that accommodate stress to incorporate component called reinforcing phase and provide a strong bond called matrix. Polymers, ceramic and metals have found application as matrix materials. The reinforcing phase is other component and is called reinforcement and can be fiber, particulate or laminar (Gupta, 2005). The composite properties depend on those of the individual components and on their interface compatibility. Many research works have been carried out to identify the parameters that govern mechanical behavior of particulate composites. Generally, it has been found that the reinforcement

effect increases with decreasing particle size and with increasing adhesion to the matrix (Marcovich *et. al*, 1998).

2.2 Matrix

In choosing to reinforce an engineering material the matrix are effectively selecting for a composite. This matrix is required to perform several functions, most of which are vital to the satisfactory performance of the composite. The matrix binds the fibers together, holding them aligned in the important stress direction. Loads are applied to the composite, are then transferred into the fibers, which constitute the principal load bearing component, through the matrix, enabling the matrix to withstand compression, flexural and shear force as well as tensile loads. The ability of composites reinforced with short or chopped fibers to support load of any kind is exclusively dependent on the presence of matrix as the load transfer medium and the efficiency of this transfer depends on the quality of the fiber-matrix bond.

The composite performance is influenced by the following matrix properties (Gupta, 2005).

- a. Elastic constants
- b. Yield and ultimate strength under tension, compression or shear
- c. Failure strain or ductility
- d. Fracture toughness
- e. Resistance to chemicals and moisture
- f. Thermal and oxidative stability

2.3 Biodegradable Composites and Packaging Film

The materials most used for food packaging are petrochemical-based polymers, due to their availability in large quantities at low cost and favorable functionality characteristics, such as, good tensile and tear strength, good barrier properties to oxygen and heat sealability (Tharanathan, 2003). However, these materials are totally non-biodegradable, leading to serious ecological problems. As a consequence, the consumer demand has shifted to eco-friendly biodegradable materials, especially from renewable agriculture by-products like chitosan, food processing industry wastes and low cost natural resources such as starch.

Although a total replacement of petroleum-based polymers by the biodegradable materials is just impossible, at least for some specific applications such as replacement seems obvious and useful. Nevertheless, such as a replacement by biodegradable materials, would allow us preserve or extend our expensive, dwindling petroleum resources. Essential prerequisites of a good packaging film (Kader, 1989) are:

- a. Allow for a slow but controlled respiration (reduces oxygen absorption) of the commodity
- b. Allow for a selective barrier to gases (Carbon Dioxide) and water vapor
- c. Creation of the modified atmosphere with respect to internal gas composition, thus regulating the ripening process and leading to shelf-life extension.
- d. Lessening the migration of lipids – of use in confectionary industry.
- e. Maintain structural integrity (delay loss of chlorophyll) and improve mechanical handling.
- f. Serve as a vehicle to incorporate food additives (flavor, colors antioxidants, and antimicrobial agent)

- g. Prevent (or reduce) microbial spoilage during extended storage.

All the above prerequisites can be met with by polymer composites, whose composition and formulation vary from commodity to commodity. Biopolymers from agricultural feed stocks and other resources have the ability upon blending and/ or processing to result in such packaging materials. Their functionality can be better expressed by using in combination with other ingredients such as plasticizers and additives. The potential uses for such biopolymeric packaging materials are:

- a. Use and throw, disposable packaging materials
- b. Routine consumer goods for day-to-day use, such as plates, cups, containers, egg boxes, etc.
- c. Disposable personal care napkins/ sanitary pads, diapers, etc
- d. Lamination coating
- e. Bags for agricultural mulching (nursery).

The most attractive feature of the biopolymer-based packaging films or composites is their total biodegradability. As a result they fit perfectly well in the ecosystem, and save our world from growing ecological pollution caused by non-biodegradable plastics, which are essentially petroleum based. A number of aerobic and anaerobic microorganisms have been identified for biodegradation. The carbon cycle involving the biopolymer degradation is shown in Figure 2.1

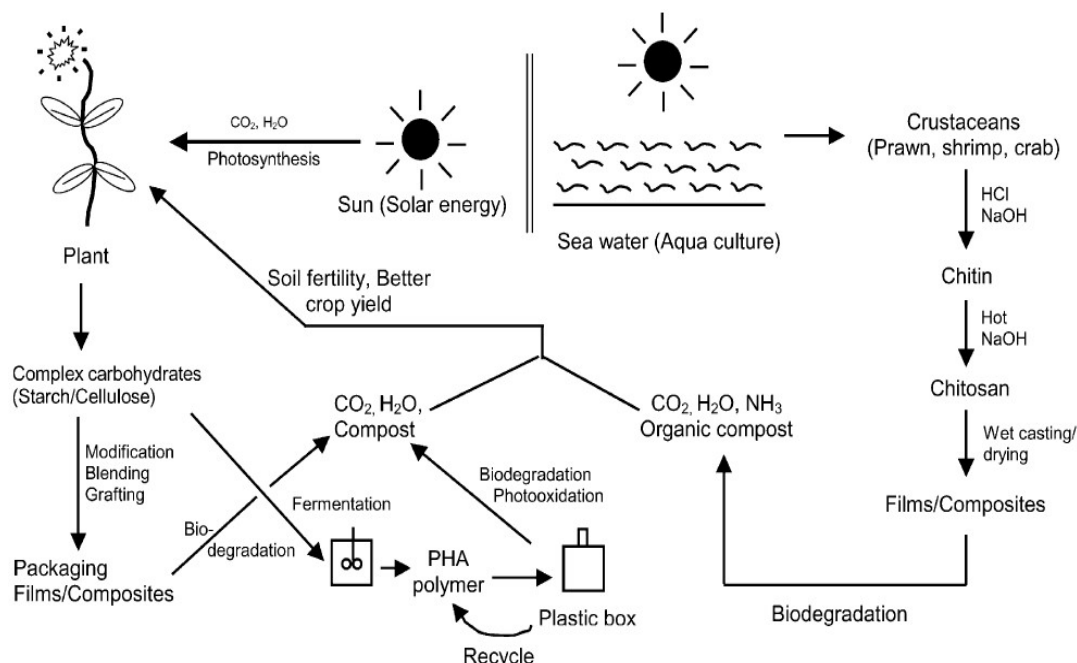


Figure 2.1: The carbon cycle of biodegradable polymers

2.4 Biodegradable Film Preparation

Two types of biomolecules, viz., hydrocolloids and lipids, are generally used in combination for the preparation of biodegradable packaging films or composites. Individually they lack structural integrity and characteristic functionality. For example, hydrocolloids, being hydrophilic are poor moisture barriers, a property compensated by adding lipids, which are very good moisture barriers. Composite films are in fact a mixture of these and other ingredients in varying proportions, which determine their barrier (to H₂O, O₂, CO₂ and aroma compounds) and other mechanical properties.

Sometimes a composite film formulation can be tailored made to suit to the needs of a specific commodity or farm produce. For example, oranges having a thick peel are prone to anaerobic conditions, which lead to an early senescence and spoilage if the composite film is rich in lipids. Phase separation encountered during the preparation of composites is overcome by using emulsifying agents. Use of plasticizers such as glycerin, ethylene glycol, sorbitol, etc. in the film formulations or composites is

advantageous to impart pliability and flexibility, which improves handling (Garcia, Martino, & Zanitzky, 2000). Use of plasticizers reduces the brittleness of the film by interfering with the hydrogen bonding between the lipid and hydrocolloid molecules.

The use of wax coating of fruits by dipping is one of the age-old methods that were in vogue in the early 12th century (Krochta, Baldwin, & Nisperos-Carriedo, 1994). This was practiced in China, essentially to retard water transpiration losses in lemon and oranges. Later fat coating of food products, specifically called “larding” was in vogue in England. Sausage casing used very commonly nowadays is nothing but a material derived from a protein source (gelatin). Usually a film thickness of ~2.5 mm is employed, and coating is done by several methods. Films are reformed thin membranous structures, which are used after being formed separately, whereas in coatings the thin film is formed directly on the commodity (R.N. Taranathan, 2003).

Dip method coating is the commonly used method for fruits, vegetables and meat products. In here the commodity is directly dipped into the composite coating formulations (in aqueous medium), removed and allowed to air dry, whereby a thin membranous film is formed over the commodity surface. Continuous dipping builds up decay organisms, soil and trash in the dipping solution, which needs to be, removed for better performance characteristics (R. N. Taranathan, 2003).

The coating can also be done by a foam application method. Emulsions are usually applied by this method. In here extensive tumbling action is necessary to break the foam for uniform distribution of the coating solution, over the commodity surface. Coating by spraying is the conventional method generally used in most of the cases. Due to high pressure (60–80 psi) less coating solution is required to give a better coverage. Programmable spray systems are available for automation during such operations (R.N. Taranathan, 2003).

Biodegradable packaging films are generally prepared by wet casting of the aqueous solution on a suitable base material and later drying. Choice of the base material is important to obtain films, which can be easily removed without any tearing and wrinkling. Infrared drying chambers are advantageous in that they hasten the drying process (Tharanathan, Srinivasa, and Ramesh, 2002). Optimum moisture content (~5–8%) is desirable in the dried film for its easy peel off from one edge of the base material.

2.5 Characterization of Biodegradable Film

There are several methods for characterize the biodegradable films which are using Atomic Force Microscopy (AFM), Fourier Transform Infrared (FTIR), Differential Scanning Calorimeter (DSC) and Thermo Gravitation Analyzer (TGA).

2.5.1 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is rather new method to characterize the surface of biodegradable film (Bining *et al.*, 1986). A sharp tip with a diameter smaller than 100 Å is scanning across a surface with a constant force. London –van der Waals interactions will occur between the atoms in the tip and the surface and these forces are detected. This will result in a line scan or profile of the surfaces (Mulder, 1996). It has emerged as the technique of choice for conducting single molecule force spectroscopy, owing largely to the limited range of forces that can be applied by competing methodologies such as the use of optical tweezers or magnetic beads (Strick *et al.*, 2003). The level of information obtained from AFM images, however, depends critically on the size, shape, and terminal functionality of the probe tips used for imaging and whether the sample consists of isolated molecules or packed molecular arrays (Engel *et al.*, 1997)